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DECOMPOSITION OF HYPOCHLORITE IN THE PRESENCE OF COPPER IN A HOMOBENEOUS MEDIUM

A.Yu. Prokopchik, Yu.P. Butkyavichyus

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16. Abstract

Spectrophotometric, spectrographic and chemical methods have demonstrated that yellow staining of a hypochlorite alkaline solution in the presence of sodium cuproate was determined by the formation of an unstable intermediate compound of trivalent copper of the type $NaCu(OH)_4$ sorium cupriate.

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DECOMPOSITION OF HYPOCHLORITE IN THE PRESENCE OF COPPER IN A HOMOGENEOUS MEDIUM

A. Yu. Prokopchik and Yu. P. Butkyavichyus

Spectrophotometric, spectrographic and chemical methods have demonstrated that yellow staining of a hypochlorite alkaline solution in the presence of sodium cuproate was determined by the formation of an unstable intermediate compound of trivalent copper of the type $NaCu(OH)_4$ sodium cupriate.

It was established that maximum light absorption of sodium cupriate is observed with wavelength 3600 ± 50 Å. It is demonstrated that trivalent copper concentration increases with a drop in temperature and solution alkalinity, and with an increase in hypochlorite and copper concentrations, as well as the ion strength of solution.

The assertion that copper is oxidized to a trivalent state /31* during catalytic decomposition of hypochlorites in the presence of copper compounds in an alkaline solution is not new [1 - 3]. However the role of the formed trivalent copper in the mechanism for catalytic decomposition of hypochlorite is still obscure. Some publications do not take into consideration trivalent copper formation at all [4]. We believe that during catalytic decomposition of copper chlorite in the presence of copper, its oxidation to the trivalent state with subsequent decomposition of the formed compound in oxygen and bivalent copper is the basis for the mechanism of this process [5, 6]. When the question is stated this way, data characterizing the formation and decomposition of trivalent copper compounds during oxidation of bivalent copper by hypochlorite are of great interest. Precisely these data are cited in this work.

Experimental Section

The technique of preparing the hypochlorite solution, and determination of its concentration are the same as in [7]. The bivalent copper solution was prepared from chemically pure recrystallized cuprous chloride.

*Numbers in margin indicate pagination in original foreign text.

Maximum light absorption of the sodium cupriate solution was determined by SF-4 spectrophotometer and ISP-28 spectrograph.

The dependence of optical density of sodium cupriate solution on different medium conditions was determined using FEKN-54 photoelectrocolorimeter. During operation of this instrument, hypochlorite optical density was compensated for by using a solution of hypochlorite of /32
the same concentration as the studied solution instead of pure solvent. In calculating the cupriate concentration from definite optical density of the solution, the sodium cupriate decimal molar extinction coefficient was assumed to be equal to 5×10^3 1/mole x cm [8].

Results of Experiments and Their Discussion

It is known that concentrated NaClO solutions are stained light yellow. Diluted solutions whose concentration is on the order 0.1 m are essentially colorless. The color does not change with strong alkylization of the solution by sodium alkali. However it is sufficient to add several drops of blue alkaline solution of sodium cuproate $Na_2Cu(OH)_4$ to this solution and the entire homogenous mixture is stained an intensive yellow.

A spectrophotometric study of the obtained solutions was made to clarify the nature of the formed yellow compound.

The SF-4 spectrophotometer revealed (see Figure 1) that in the area of wavelengths 3600 Å a characteristic maximum light absorption is observed. Light absorption in this area, as is apparent from Figure 2, rises with an increase in copper concentration in solution. It should be noted that with an increased hypochlorite concentration (see Figure 2, curve 6), the area of intensive light absorption by hypochlorite itself expands so much that the area of light absorption we are interested in is completely overlapped. The bivalent copper solution does not absorb light in our studied area.

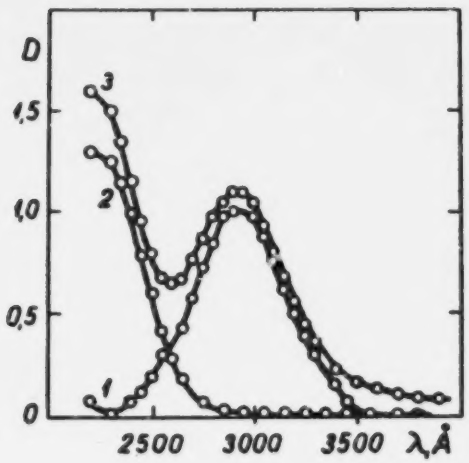

Figure 1. Optical Density of Individual Solution and Mixture of Hypochlorite with Sodium Cuproate
Concentrations of solutions in m:
1. NaClO 0.03,
2. Cu 3×10^{-3}
3. NaClO 0.03, Cu 3×10^{-3}
Thickness of the layer is 1 mm. Room temperature, solution alkalinity 1 n. NaOH.

In order to show that the observed absorption at 3600 Å belongs precisely to trivalent copper and is not linked to hypochlorite, a study was made of light-absorption of a solution containing only specially electrochemically prepared trivalent copper [9]. It was obtained by anode oxidation of a copper plate in 0.5 m NaOH solution. Anode current density was 30 - 40 a/in^2, synthesis temperature was about -3°C, electrolysis lasted 0.5 - 1.5 min, the cathode was a platinum /33 wire separated from the anode space by glass filter #2. As a result of electrolysis an intensively yellow solution of sodium cupriate $NaCu(OH)_4$ was produced.

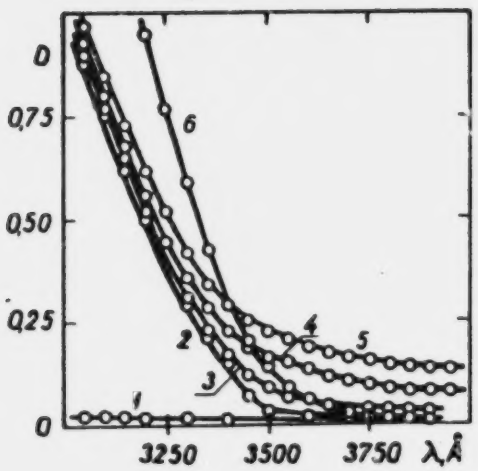

Figure 2. Dependence of Optical Density of Solution on Component Concentration
Concentrations of solutions in m:
1. Cu 3 x 10^{-3},
2. NaClO 0.03
3-5. NaClO 0.03 and copper respectively 1.5, 3 and 6 x 10^{-3},
6. NaClO 0.06
The layer is 1 m thick, room temperature, solution alkalinity 1 n NaOH

Study of absorption of the sodium cupriate solution obtained by this method confirmed our hypothesis that there is an absorption maximum in the area 3500 - 3800 Å. SF-4 could not determine more accurately the wavelength corresponding to the absorption maximum because of rapid decomposition of sodium cupriate At room temperature $NaCu(OH)_4$ decomposed in solution in several minutes, and its decomposition products are blue sodium cuproate $Na_2Cu(OH)_4$ and gaseous oxygen.

It is easy to judge the instability of sodium cupriate from the data presented in Figure 3 (see curves 2 and 2a). Nevertheless, an

absorption maximum in the area of 3500 - 3800 Å is indisputable. After decomposition of cupriate, absorption is only observed in an area characteristic for bivalent copper (compare curves 1 and 1a).

The method of photographing the iron emission spectrum of the ISP-28 spectrograph through a quartz cell with solution of anode-synthesized sodium cupriate was used for more precise detection and determination of the maximum observed light absorption. Photographs were taken every 30 sec for 9.5 min (during this time trivalent copper is completely decomposed). By constriction in the absorption band maximum it was thus stated that the trivalent copper absorption maximum corresponds to wavelength 3600 ± 50 Å.

The presence of trivalent copper in a homogeneous solution containing sodium cuproate and hypochlorite was also chemically confirmed. /34 According to published data [10] barium ions were used to isolate from the aforementioned mixture an insoluble dark red sediment of trivalent copper-barium cupriate compound of gross composition $Ba(CuO_2)_2$. It should be noted that barium cupriate is not immediately released from solution, but only at the end of a certain time. Analysis of the sediment was made by iodometric method from [2, 3].

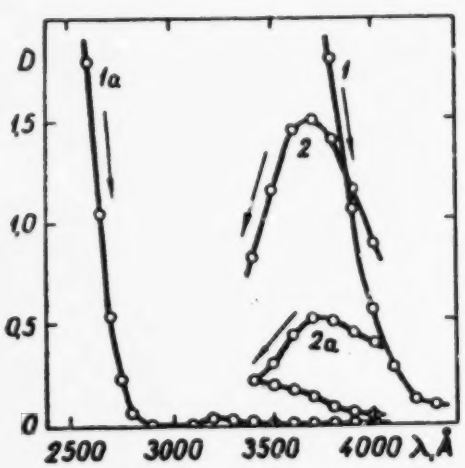

Figure 3. Optical Density of Solutions of Electrochemically Prepared Sodium Cupriate in 0.5 m Solution of NaOH. (Key next page)

Figure 3. Key:
1,2. optical density of freshly prepared solutions
1a, 2a. optical density of the same solutions respectively at the end of 5 and 2 min
Thickness of the layer 1 mm, room temperature. The arrows indicate the sequence of the measurements.

Further experiments to determine dependence of trivalent copper concentration on different medium factors were conducted using the FEKN-54 photoelectrocolorimeter with light filter and maximum transmission at 3600 Å.

As is apparent from Figure 4, the solution optical density rises with an increase in hypochlorite concentration. We are easily convinced that the actual dependence of cupriate concentration on hypochlorite concentration changes with an alteration in a concentration of the latter. Whereas up to concentration of NaClO on the order 0.15 m, this dependence can be considered linear without particular error, with further increase in NaClO concentration it becomes fractional, less than 1. One can hypothesize that with a rise in NaClO concentration the degree of copper oxidation in solution must approach a constant quantity, under definite conditions approaching 100%. Our experiments determining the kinetic order of the hypochlorite decomposition reaction in the presence of cuproate whose results are presented in Figure 5 confirm this hypothesis.

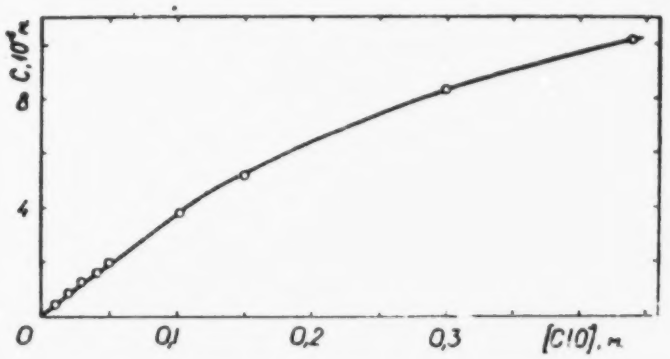

Figure 4. Dependence of Equilibrium Concentration of Cupriate on Hypochlorite Concentration
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Figure 4. Continued:
Alkalinity of the mixture is about 0.5 n NaOH, total copper concentration in solution is 4 x 10^{-4} m, temperature is about 20°C.

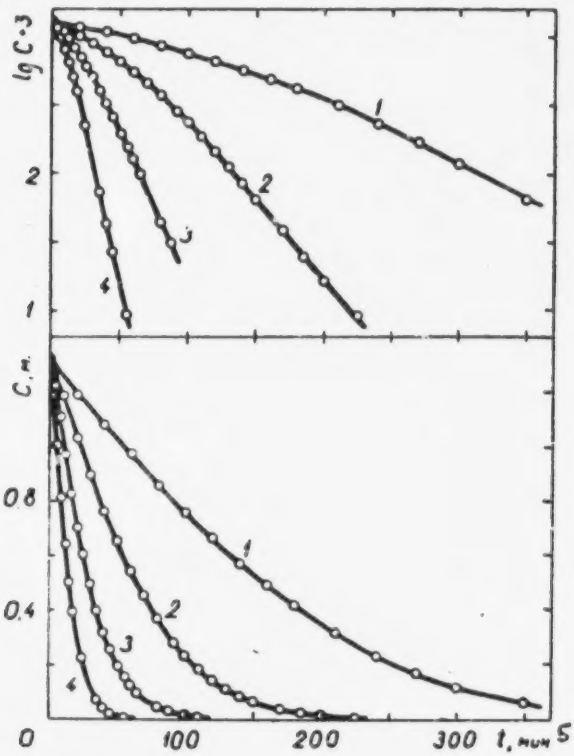

Figure 5. Velocity and Order of Catalytic Decomposition of NaClO in the Presence of Sodium Cuproate with Different Temperatures:

1. 40
2. 50
3. 60
4. 70°C
5. min

Alkalinity of the solutions is about 1 n NaOh, total copper concentration is 9.45 x 10^{-4} m, ion strength of solution $\mu \simeq 5$ (because of considerable NaCl content).

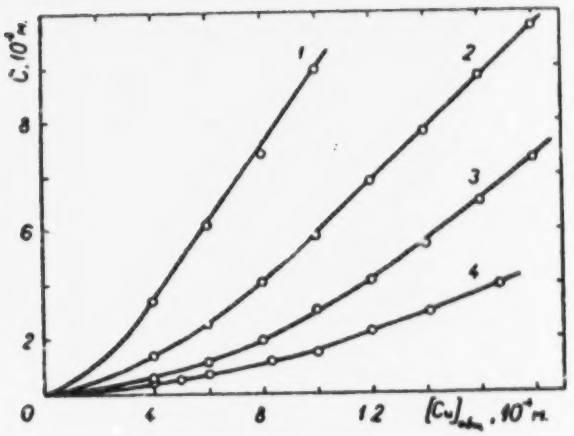

Figure 6. Dependence of Cupriate Equilibrium Concentration on Alkalinity of Hypochlorite and Cuproate Mixture
1. is about 0.5
2. is about 1.0
3. is about 1.5.
4. is about 2.0 n NaOH
Experimental temperature is 17°C, NaClO concentration is 0.1 m.

As is apparent from this figure, decomposition of 1.3 m of hypochlorite solution occurs by kinetic order close to zero, which indicates the constant concentration of the decomposing trivalent copper, i.e., it essentially does not depend on the hypochlorite concentration. Decomposition of the diluted NaCl O solutions ($\lesssim$ 0.3 m), as is also apparent from Figure 5, occurs precisely by the first order, leading to a linear dependence of trivalent copper concentration on hypochlorite concentration. The first order of the decomposition reaction of diluted hypochlorite solution (on the order 0.1 n) in the presence of cuproate was also observed by Zenker [4].

With an increase in copper concentration in solution (see Figure 6), its optical density increases, the rise in solution alkalinity results in a sharp decrease in optical density, i.e., the trivalent copper equilibrium concentration in solution diminishes. The latter

must influence the hypochlorite decomposition velocity in the presence of copper, i.e., with a rise in solution alkalinity it must slow down. In order to verify this hypothesis, we conducted special experiments whose results are presented in Figure 7. As is apparent from this figure, the velocity of studied hypochlorite decomposition diminishes with a rise in solution alkalinity, which agrees with the data of Zenker [4].

Addition of sodium alkali increases the ion strength of the solution, which must influence the hypochlorite decomposition rate. Experiments in solutions with different ion strength (see Figure 8) demonstrated that increase in solution ion strength accelerates hypochlorite composition. Consequently, increase in alkali concentration slows down the decomposition more strongly than is accelerated by the rise in ion strength of the solution. In light of these data it is difficult to understand Lister's [1] statement that this reaction does not depend on alkalinity of the medium.

Further experiments demonstrated that increase in hypochlorite decomposition velocity with an increase in solution of ion strength is linked to an increase in the trivalent copper equilibrium concentration in solution. One can easily be convinced of this from the data presented in Figure 9.

The dependence of equilibrium concentration of cupriate on temperature was also defined. As is apparent from Figure 10, with a rise in temperature, the cupriate concentration drops.

The nonlinear relationships presented in Figure 6 can be transformed into linear by taking the logarithm of the experimental data. They are presented in this form in Figure 11 and can be employed for /39
extrapolation analysis of trivalent copper concentration with low initial cuproate concentrations.

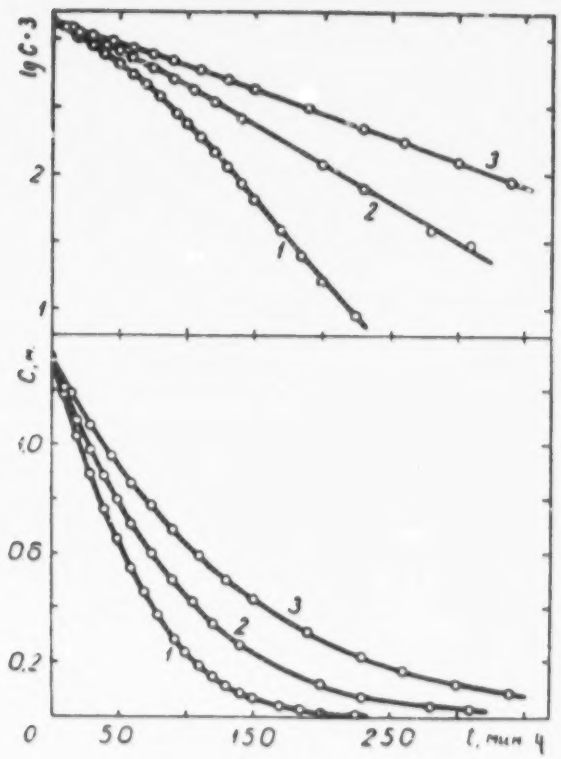

Figure 7. Dependence of Rate of Catalytic Decomposition of NaClO in the Presence of Sodium Cuproate on Alkalinity of the Medium

1. 0.98
2. 1.88
3. 2.93 n of NaOH 4. min.

Total copper concentration is 9.45×10^{-4} m, experimental temperature is 50°C, ion strength of solutions μ: 1 is about 4.9, 2 is about 5.8, 3 is about 6.9 (because of the considerable NaCl content)

Based on all of these experimental data one can state that catalytic decomposition of sodium hypochlorite in the presence of homogenously dissolved copper hydroxide is directly linked to the formation and decomposition of a trivalent copper compound, sodium cupriate.

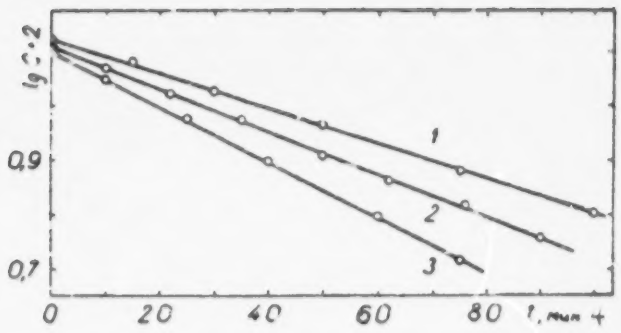

Figure 8. Dependence of Rate of Catalytic Decomposition of NaClO in the Presence of Sodium Cuproate on Ion Strength of Solution μ:

1. 1.34
2. 2.67
3. 4.15 4. min.

Experimental temperature is 40°C, total copper concentration is 9.45×10^{-5} m, alkalinity is about 1.0 n NaOH, initially concentration of NaClO is about 0.13 n (increase in ion strength because of addition of NaCl)

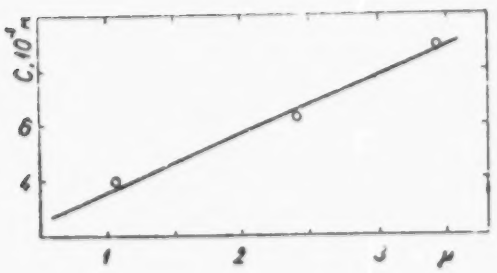

Figure 9. Dependence of Equilibrium Concentration of Cupriate on Ion Strength of Solution.

(continued next page)

Figure 9. Continued:
Experimental temperature is about 22°C, concentration of NaClO is 0.1 m, solution alkalinity is 0.96 n. NaOH, total copper concentration is 1 x 10^{-3} m (increase in ion strength because of addition of NaCl).

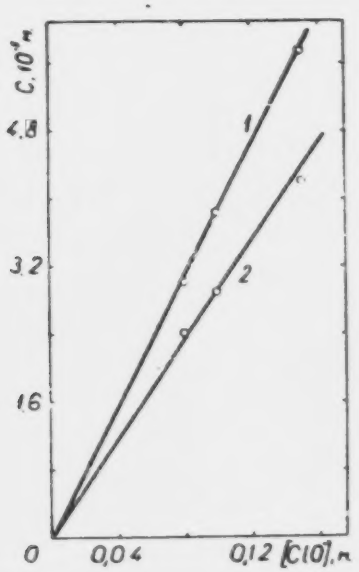

Figure 10. Dependence of Equilibrium Concentration of Cupriate on Temperature of Hypochlorite and Cuproate Mixture

1. 10
2. 30°C

Total copper concentration is 4 x 10^{-4} m, alkalinity of the medium is 0.5 n NaOH

Information about the mechanism for this process is cited in an individual article [6].

We are grateful to colleagues of our institute G. R. Rozovskiy and Z. B. Alauna for help in preparing the trivalent copper solution by anode method and making the spectral measurements.

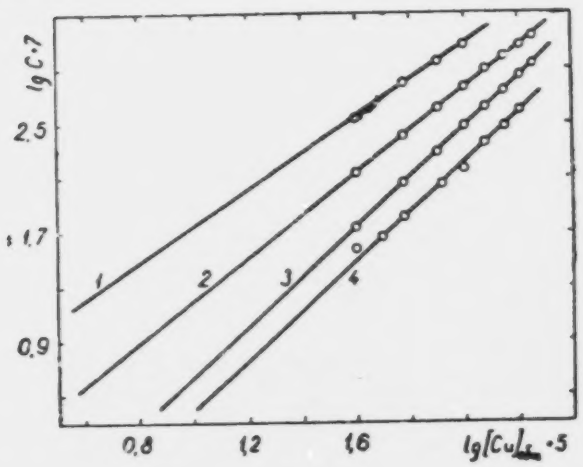

Figure 11. Logarithmic Transformation of Relationships Presented in Figure 6.

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